

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 511 541 A1

(12)

EUROPEAN PATENT APPLICATION(21) Application number: **92106384.8**

(51) Int. Cl.⁵: **A01N 51/00, A01N 43/86,
A01N 43/50, A01N 43/78,
A01N 43/54, B27K 3/34**

(22) Date of filing: **14.04.92**

(30) Priority: **27.04.91 JP 125172/91
12.12.91 JP 350751/91**

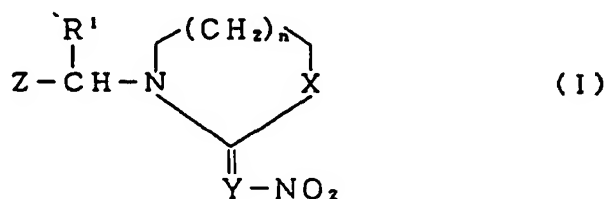
(43) Date of publication of application:
04.11.92 Bulletin 92/45

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI LU NL SE

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(54) **Agents for preserving technical materials against insects.**(57) **The use of the compounds of the formula (I)**

as agents for preserving technical materials against insects.

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The present invention relates to the use of known nitromethylene or nitroimino compounds as agents for combating technical materials destroying insects in order to preserve these materials.

The present invention also relates to compositions useful for combating these insects, preserving technical materials completely, i.e. not only against insects but also against fungi, bacteriae and algae and for treating soil to protect technical materials against termite infestations.

The invention furthermore relates to processes for treating technical materials and for soil treatment against termite infestations.

The compounds and their insecticidal use in the field of plant protection has already been known. Compare for example with EP-A 163855 and EP-A 192060.

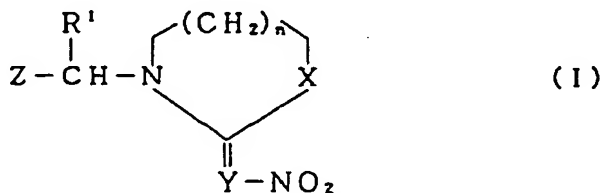
Insecticidal agents and compositions of said compounds and their use to preserve technical materials completely and to treat soil against-termite infestations have not been known up to now.

Different insects are known as pests infesting technical materials so that due to serious damages caused thereby undesirable effects on living environment and cultural assets principally made of these materials have posed a social problem, urgently requiring effective controlling of the pests. Termites are known as important examples of these pests.

At present, use for combating technical materials destroying insects has been made of organophosphorus insecticides such as phoxim [0-(α -cyanobenzylideneamino)0,0-diethylphosphorothioate], chloropyrifos [0,0-diethyl-3,5,6-trichloro-2-pyridylphosphorothioate], etc., as well as pyrethroides series insecticides such as permethrin [5-benzyl-3-furylmethyl-3-(2-methoxy-carbonyl-1-propenyl)-2,2-dimethyl-cyclopropane carboxylate], decamethrin [α -cyano-3-phenoxybenzyl d,l-cis-3-(2,2-dibromovinyl)-2,2-dimethyl cyclopropane carboxylate], cypermethrin [α -cyano-3-phenoxybenzyl (\pm) cis, trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate], fenvalerate [(RS)- α -cyano-3-phenoxybenzyl (RS)-2-(4-chlorophenyl)-3-methylbutyrate], cyflutrine [cyano-(4-fluoro-3-phenoxyphenyl) methyl-3-(2,2-dichloroethenyl)-2,2-dimethyl-cyclopropane carboxylate].

However, the above-mentioned insecticides are unsatisfactory as far as effective concentration and the long lasting effect are concerned.

It has been found that the known compounds of the formula (I)



wherein X is NH or S,

Y is CH or N

Z is 2-chloro-5-pyridyl or 2-chloro-5-thiazolyl,

R¹ is hydrogen or methyl, and

n is 0 or 1,

exhibit powerful insecticidal properties on material destroying insects and preferably on termites.

The compounds according to the invention of the formula (I) surprisingly exhibit an extremely strong insecticidal action on material destroying insects and the function is substantially superior to that of known insecticidal agents.

The compounds of the formula (I) can be used to preserve technical materials against insects.

In the formula (I), the individual residues have the following preferable meanings:

X is NH or S,

Y is CH or N,

Z is 2-chloro-5-pyridyl,

R¹ is hydrogen, and

n is 0 or 1.

As examples of the active substances to be used according to the invention, the following ones are particularly preferred:

1-(6-chloro-3-pyridylmethyl)-2-nitromethyleneimidazolidin ,

3-(6-chloro-3-pyridylmethyl)-2-nitromethylenethiazolidine,

1-(6-chloro-3-pyridylmethyl)-2-nitroiminoimidazolidine,

1-(6-chloro-3-pyridylmethyl)-2-nitromethylenetetrahydropyrimidine, and
3-(6-chloro-3-pyridylmethyl)-2-nitromethylenetetrahydro-2H-1,3-thiazine.

The active substances to be used according to the invention exhibit powerful insecticidal effects against material destroying insects.

5 They can therefore be used in insecticidal agents for combating material destroying insects and preserving technical materials. They can also be used for soil treatment against termite infestation.

As individual examples of technical materials preserved by means of the insecticidal agents according to the present invention the following ones can be mentioned: wood or composite wood-materials (such as pressed wood, particle board, chip board, wafer board, plywood, wood laminated material, freshly cut
10 timber/lumber etc.), paper, leather or leather products, natural or synthetic polymers, textiles.

Preferable materials are wood or composite wood-materials.

As individual examples of insects to be combated or controlled by the active substances of formula (I) according to the present invention the following ones can be mentioned:

15 Order Isoptera

Mastotermitidae

Kalotermitidae such as Kaloterms spp.
Cryptoterms spp. etc.

20 Termopsidae such as Zootermopsis spp. etc.

Rhinotermitidae such as Reticuliterms spp.
Heteroterms spp.
Coptoterms spp. etc.

25 Termitidae such as Amiterms spp.
Nasutiterms spp.
Acanthoterms spp.
Mikrotermes spp. etc.

30 Order Coleoptera

Lyctidae such as Lyctus brunneus etc.
Bostrychidae such as Bostrychus capucinus
Dinoderus minutus etc.

35 Anobiidae such as Anobium punctatum
Xyletinus peltatus
Xestobium rufovillosum
Ptilinus pectinicomis etc.
Cerambycidae such as Hylotrupes bajulus
40 Hesperophanus cinereus
Stromatium fulvum
Chlorophorus pilosus etc.

Oedemeridae

Serropulpidae

45 Curculionidae

Seolytida

Platypodidae

Order Hymenoptera

50

Siricidae such as Sirex spp.
Urocerus spp.

Formicidae such as Camponotus spp.

In the above Isopterous insects, especially, there may be mentioned as examples of termites in Japan:

55 Deucotermes sp. ratur,
Coptoterms formosanus,
Glyptoterms fucus,
Glyptoterms satsumensis,

Glyptotermes nakajimai,
 Glyptotermes Kodamai,
 Incisitermes minor,
 Neotermes koshunensis,
 5 Cryptotermes domesticus,
 Hodotermopsis japonica,
 Reticulitermes miyatakei,
 Odontotermes formosanus,
 Nasutitermes takasagoensis,
 10 Capritermes nitobei and so on.

The active compounds of the general formula (I) in the present invention can be prepared into the customary formulations, such as solutions, emulsions, suspensions, powders, foams, pastes, granules, aerosols, natural and synthetic materials impregnated with active compounds, and micro-capsules.

These formulations may be produced in a known manner, for example, by mixing the active compounds
 15 with extenders, that is to say liquid or liquefied gaseous or solid diluents or carriers, optionally with the use of surface-active agents, that is to say emulsifying agents, dispersing agents, and/or foam-forming agents. In the case of using water as an extender, organic solvents can, for example, also be used as auxiliary solvents.

As liquid diluents or carriers can be mentioned, for example, aromatic hydrocarbons, such as xylene,
 20 toluene and alkyl naphthalenes, chlorinated aromatic or chlorinated aliphatic hydrocarbons, such as chlorobenzenes, chloroethylenes and methylene chloride, aliphatic or alicyclic hydrocarbons, such as cyclohexane or paraffins, for example, mineral oil fractions, alcohols, such as butanol or glycol as well as their ethers and esters, ketones, such as acetone, methyl ethyl ketone, methyl isobutyl ketone or cyclohexanone, or strongly polar solvents, such as dimethylformamide and dimethylsulfoxide, as well as
 25 water.

By liquefied gaseous diluents or carriers are meant liquids which are gaseous at normal temperature and under normal pressure, for example, aerosol propellants, such as halogenated hydrocarbons as well as butane, propane, nitrogen and carbon dioxide.

As solid diluents there may be used ground natural minerals, such as kaolins, clays, talc, chalk, quartz,
 30 attapulgite, montmorillonite or diatomaceous earth, and ground synthetic minerals, such as highly-dispersed silicic acid, alumina and silicates.

As solid carriers for granules there may be used crushed and fractionated natural rocks such as calcite, marble, pumice, sepiolite and dolomite, as well as synthetic granules of inorganic and organic meals, and granules of organic material such as sawdust, coconut shells, maize cobs and tobacco stalks.

As emulsifying and/or foam-forming agents there may be used nonionic and ionic emulsifiers, such as
 35 polyoxyethylene-fatty acid esters, polyoxyethylene-fatty alcohol ethers, for example, alkylaryl polyglycol ethers, alkylsulfonates, arylsulfonates as well as albumin hydrolysis products. Dispersing agents include, for example, lignin sulfite waste liquors and methyl cellulose.

Adhesives such as carboxymethyl cellulose and natural and synthetic polymers, (such as gum arabic,
 40 polyvinyl alcohol and polyvinyl acetate) can be used in the formulations in the form of powders, granules or emulsifiable concentrations.

It is possible to use colorants such as inorganic pigments, for example, iron oxide, titanium oxide and Prussian Blue, and organic dyestuffs, such as alizarin dyestuffs, azo dyestuffs or metal phthalocyanine
 45 dyestuffs, and trace elements, such as salts of iron, manganese, boron, copper, cobalt, molybdenum and zinc.

The formulations, in general, contain from 0.001 to 95 percent by weight of active compound, preferably from 0.5 to 90 percent by weight.

Furthermore, the active compound of the present invention having the formula (I) can be present as a mixture with a synergist in a formulation or a use form, of the type that is commercially useful. The term
 50 "synergist" denotes a compound which is not active in itself, but promotes the action of an active compound. The content of the active compounds having the general formula (I) of the present invention in commercially useful formulations can vary within a wide range. The active compound concentration of the formulation for use is, for example, from 0.0000001 to 100 percent by weight, preferably from 0.0001 to 1 percent by weight.

In order to protect the above-mentioned materials completely, i.e. not only against material destroying
 55 insects but also against fungi, bacteria and algae, they can be treated with compositions containing at least one insecticidally active compound of the formula (I) and at least one biological active fungicide, bactericide or algicide.

Wood or composite wood-materials can preferably be treated with a composition containing
 a) an insecticidally effective amount of a compound of the formula (I) or mixtures thereof and
 b) a fungicidally effective amount of at least one compound selected from the group of
Trihalosulphenyl-Compounds such as

- 5 - N-Dichlorofluoromethylthio-N',N'-dimethyl-N-phenylsulfuric acid diamide (Dichlofluanide)
- N-Dichlorofluoromethylthio-N',N'-dimethyl-N-p-toluylsulphamide (Tolyfluanide)
- N-Trichloromethylthiophthalimide (Folpet)
- N-Dichlorofluoromethylthiophthalimide (Fluorfolpet) etc.

Iodine-Compounds such as

- 10 - 3-Iodo-2-propynyl-butylcarbamate (IPBC)
- 3-Iodo-2-propynyl-hexylcarbamate
- 3-Iodo-2-propynyl-cyclohexylcarbamate
- 3-Iodo-2-propynyl-phenylcarbamate
- Diiodomethyl-p-tolylsulphone (Amical 48) etc.

15 Phenols such as

- ortho-Phenylphenol
- Tribromophenol
- Tetrachlorophenol
- Pentachlorophenol etc.

20 Azole-Compounds such as

- 1-(4-Chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4 triazol-1-yl)-2-butanone (Triadimefon)
- β -(4-Chlorophenoxy)- α -(1,1 dimethyl-ethyl)-1H-1,2,4 triazole-1-ethanol (Triadimenol)
- $\pm\alpha$ [2-(4-chlorophenyl) ethyl]- α -(1,1-dimethylethyl)-1H-1,2,4-triazole-1-ethanol (Tebuconazole)
- 1-[2(2,4-dichlorophenyl) 4-propyl-1,3-dioxolan-2-ylmethyl]-1H-1,2,4-triazole (Propiconazole)
- 25 - 1-[2(2,4-dichlorophenyl)-1,3-dioxolan-2-ylmethyl]-1H-1,2,4-triazole (Azaconazol)
- (RS)-2(2,4-dichlorophenyl)-1-(1H-1,2,4 triazol-2-yl)-2-ol (Hexaconazol)
- 1-N-propyl-N-[2-(2,4,6-trichlorophenoxy) ethyl] carbamoylimidazol (Prochloraz) etc.

Tin Compounds such as

- Tributyl tin octoate
- 30 - Tributyl tin oleate
- Bistibutyl tin oxide
- Tributyl tin naphthenate
- Tributyl tin phosphate
- Tributyl tin benzoate etc.

35 Thiocyanate Compounds such as

- Methylenebisthiocyanate (MBT)
- 2-Thiocyanomethylthiobenzothiazole (TCMTB) etc.

Quaternary Ammonium Compounds such as

- Benzyl-dimethyl-tetradecylammoniumchloride
- 40 - Benzyl-dimethyl-dodecylammoniumchloride etc.

Benzimidazole Compounds such as

- 2-(2'-Furyl)-1H-benzimidazole (Fuberidazole)
- Methylbenzimidazol-2-ylcarbamate (BCM)
- 2-(4'-thiazolyl) benzimidazole (Thiabendazole)
- 45 - Methyl (1-butylcarbamoyl)-2-benzimidazole carbamate (Benomyl)

Isothiazolinone Compounds such as

- N-Methylisothiazolin-3-one
- 5-Chloro-N-methylisothiazolin-3-one
- 4,5-Dichloro-N-octylisothiazolin-3-one
- 50 - N-Octylisothiazolin-3-one

Morpholine Compounds such as

- C₁₄-C₁₁-4-Alkyl-2,6-dimethylmorpholine (Tridemorph)

Pyridine Compounds such as

- 1-Hydroxy-2-pyridine-thione and Sodium Iron, Manganese or Zinc-Salt thereof
- 55 - Tetrachloro-4-methyl sulphonyl pyridine

N-Cyclohexyldiaziniumdioxy Compounds such as

- Tris-(N-cyclohexyldiaziniumdioxy) aluminium
- Bis-(N-cyclohexyldiaziniumdioxy) copper

Naphthenate Compounds such as

- Zinchnaphthenate

Quinoline Compounds such as the copper salt of

- 8-hydroxy-quinoline

Nitriles such as

- 1,2,3,5-Tetrachloro-4,6-cyanobenzene.

Boric compounds such as boric acid, borax, borates

Ureas such as N'(3,4-dichlorophenyl)-N,N-dimethylurea

Furane derivatives such as Fumecyclo

These fungicidally effective compounds are added to the composition in order to prevent wood or wood materials not only against wood destroying insects but also against

- Wood-discoloring fungi such as

Ascomycetes (Caratocystis minor)

Deuteromycetes (Aspergillus niger, Aureobasidium pullulans, Dactyleum fusarioides, Penicillium

Variabile, Sclerophoma pithyophila, Scopularia phycomyces, Trichoderma viride, Trichoderma

liguorum)

Zygomycetes (Mucor spinosus)

and/or

- Wood-destroying fungi such as

Ascomycetes (Chetomium alba-arenulum, Chaetomium globosum, Humicola grisea, Petriella setifera,

Trichurus spiralis)

Basidiomycetes

(Coniophera puteana

Coriolus versicolor

Donbiopora expansa

Glenospora graphii

Gloeophyllum abietinum

Gloeophyllum adorum

Gloeophyllum protactum

Gloeophyllum trabeum

Gloeophyllum sepiarium

Lentinus cyathioformes

Lentinus edodes

Lentinus lepideus

Lentinus squavrolousus

Paxillus panuoides

Pleurotus ostreatus

Poria placenta

Poria monticola

Poria vaillantii

Poria vaporea

Serpula himantoides

Serpula lacrymans

Tyromyces palustris)

Deuteromycetes (Cladosporium herbarum).

Generally the compositions also will include at least one additional diluent, emulsifier, melting agent, organic binding agent, auxiliary solvents, processing additives, fixatives, plasticizers, UV-stabilizers or stability enhancers, dyes (water soluble, water insoluble), color pigments, siccatives, corrosion inhibitors, antiseptant agents, additional insecticides (such as insecticidal carbamates, organophosphorus compounds, halogenated hydrocarbons, pyrethroids etc.), anti skinning agents and the like.

The above-mentioned additional ingredients and their use are described in prior art. (EP-A 0370665, DE-A 3531257, DE-A 3414244).

The compositions according to the present invention generally comprise from about 10^{-6} to 30 parts by weight, preferably from about 0.0005 to 15 parts by weight and more preferably from 0.005 to 2 parts by weight of the insecticide of formula (I) and from 0.01 to 90 parts by weight, preferably from about 0.05 to 50 parts by weight and more preferably from 0.1 to 30 parts by weight of at least one of the above-mentioned fungicides.

The compositions can be provided as ready for use products or as concentrates, which have to be

diluted prior to use.

The compositions can be applied by means of brushing, spraying, dipping, double vacuum and the like as known in the art. The compositions can be prepared by any technique known in the art.

The content of the present invention will be concretely explained by way of the following examples but the present invention should not be limited only thereto.

Examples for compositions:

*Remark: the percentages are given in percent by weight

Example 1

0.005%	1-(6-chloro-3-pyridylmethyl)-2-nitroiminoimidazolidine (imidacloprid)
5 %	Butylglycol
94.995%	Mineral spirits

Example 2 Impregnating agent/Primer

0.01 %	Imidacloprid
0.5 %	Dichlofluanide
1. %	Tebuconazole
9.7 %	Alkyd resin (solid)
88.79 %	Mineral spirits

Example 3 Wood stain/low build

0.01 %	imidacloprid
0.5 %	Dichlofluanide
1.2 %	Tebuconazole
21 %	Alkyd resin (solid)
2 %	Pigment
4 %	Antisettlement additive, dryes etc.
71.29%	Mineral spirits

Example 4 Wood stain/high build

0.015%	imidacloprid
0.6 %	Dichlofluanide
1.5 %	Tebuconazole
40 %	Alkyd resin
2 %	Pigment
4 %	Antisettlement additive, dryer etc.
48.115%	Mineral spirits

Example 5 Soil treatment

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20 %	imidacloprid
8 %	ethylene glycol
3 %	emulsifiers
0.25 %	thickeners
68.75 %	distilled water

Example 6 Wood brushing

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0.1 %	imidacloprid
1 %	3-bromo-2,3-diiodo-2-propenyl ethylcarbonate
98.9 %	organic solvents

Example 7 wood brushing

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0.1 %	imidacloprid
1.5 %	4-chlorophenyl-3-iodopropargylformal
98.4 %	organic solvents

Example 8 Formicidal test

Compounds under test

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Examples of the active compounds according to the present invention

I.1: 1-(6-chloro-3-pyridylmethyl)-2-nitromethyleneimidazolidine

I.2: 3-(6-chloro-3-pyridylmethyl)-2-nitromethylenethiazolidine

I.3: imidacloprid

35

Comparative compounds

A : phoxim

B : chlorpyrifos

40

Preparation of test formulation:

Solvent: 3 parts by weight of xylene

Emulsifier: 1 part by weight of polyoxyethylene-alkylphenyl-ether

45

To prepare a suitable formulation of the active compound, 1 part by weight of each of the active compounds was mixed with the above-mentioned amount of the solvent containing the above-mentioned amount of the emulsifier, and the mixture was diluted with water to a predetermined concentration.

Test method:

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1 ml of the aqueous solution prepared in the above-mentioned procedure was uniformly applied using a pipette onto a filter paper that was placed in petri dish of 9 cm diameter. Ten head of worker termites (*Coptotermes formosanus*) were replaced into the petri dish and it was kept in a constant temperature chamber at 25° C.

55

After four days, the mortality of the termites was investigated. This test procedure was carried out in duplicate per each concentration of the active compounds under test.

The test results are shown in Table 1.

Table 1

Compound	Concentration of active compound (ppm)	Mortality of termites after four days (%)
I.1	40	100
	8	100
	1.6	100
	0.32	100
I.2	40	100
	8	100
	1.6	100
	0.32	100
I.3	40	100
	8	100
	1.6	100
	0.32	100
A	40	100
	8	100
	1.6	100
	0.32	90
B	40	100
	8	100
	1.6	100
	0.32	100
Untreated		0

Example 9 Test on Residual Effect

Small blocks of Japanese redpine tree (2 cm x 2 cm x 2 cm) were soaked for one minute into the aqueous solution prepared by the similar procedure to Example 8.

After air-dried, they were kept in a constant temperature chamber at 40 °C for four weeks. Then each of the thus treated blocks was placed in a polymeric cup (10 cm diameter) containing 150 ml of sandy loam of 20 % moisture content. Into each of the polymeric cups, 100 head of working termites and 10 head of soldier termites (*Coptotermes formosanus*) were released. After three weeks, the degree of xylophagous damage in the block and the mortality of the termites were investigated.

Three tests were carried out in duplicate 25 °C, and the results are shown in Table 2.

The index of xylophagous damage observed on the test blocks:

- 0 : No damage
- 0.5 : One to two traces of damage each having a depth of about 1 mm from the block surface
- 1 : One to two evident damages each having a depth from 1 to 2 mm from the block surface
- 2 : More than three evident damages or more than one deep trace of damage having a depth of more than 2 mm from the block surface
- 3 : More than three deep damages
- 4 : Evidently damaged zone covering up to about one third of the whole surface area of the block
- 5 : Evidently damaged zone covering more than one third of the whole surface area of the block

Table 2

Compound	Concentration of active compound (ppm)	Mortality termites after three weeks (%)	Degree of xylophagous damage in the pine tree block (0 - 5)
I.1	40	100	0
	8	100	0
	1.6	100	0
	0.32	98	0.5
I.2	40	100	0
	8	100	0
	1.6	100	0
	0.32	100	0
I.3	40	100	0
	8	100	0
	1.6	100	0
	0.32	100	0
A	40	25	3
	8	0	5
	1.6	0	5
	0.32	0	5
B	40	100	0
	8	78	1
	1.6	0	3
	0.32	0	5
Untreated		0	5

Example 10 Toxic value against larvae of *Hyloterpes bajulus*

The toxicity against larvae of *Hyloterpes bajulus*, using wood samples treated with the active compound I.3 provided in Example 8 in chloroform having concentrations of 1.44×10^{-5} %, 1.44×10^{-4} %, 7.2×10^{-3} %, and 1.44×10^{-2} % was determined according to the detailed description of DIN EN 47 (edition 1990, Beuth Verlag GMBH) which is concerned with the European standard method prescribed by the European Committee for standardization concerning wood preservatives, determination of the toxic value against larvae of *Hyloterpes bajulus*.

An outline of the method is as follows: (see DIN EN 47 for detail)

Five wood-samples (50 mm x 25 mm x 15 mm) which are treated by the active compound beforehand (impregnation treatment in vacuum) are provided and in each specimen, a regular pattern of six holes are bored, and then one head of the larvae is inserted per a hole.

After four weeks, the specimens are cut up in turn and the number of live/dead of larvae is determined.

In determination, where a live larvae is identified in a specimen, then the remaining specimens without cutting up are stored for a further eight weeks, and afterword, the number of live/dead larvae is determined.

From this test, the Toxic threshold value was between 1.08 g/m^3 and 10.8 g/m^3 of the active compound I.3.

The results are shown in Table 3.

Table 3

Duration of the test in weeks	Concentration of the impregnating solution (%)	Quantity of active compound concentrate absorbed in g/m ³ wood			State of the larvae at the end of the test			
		min.	max.	M-value	dead no wood digested	dead wood digested	living	not found
4	0.0144	82.08	116.64	103.97	27	3	0	0
	0.0072	45.36	56.88	52.85	29	1	0	0
	0.00144	10.08	11.23	10.80	4	6	1 (*1)	1
12	0.00144 (*2)	9.94	11.66	10.80	6	11	0	1
	0.000144	0.95	1.21	1.08	4	12	11	3
	0.0000144	0.09	0.12	0.11	1	4	23	2
12	control samples	impregnated with chloroform			2	2	24	2
		not treated			1	1	27	1

Note:

(*1) One live larvae was found in the second specimen.

(*2) The remaining three specimens were tested for further eight weeks (12 weeks in total).

Comparative values of W. Metzner et al in "Holz als Roh- und Werkstoff, 35 (1977) 233-237", table 6 on page 236.

Table 4

Insecticide	toxic value (g/m ³)	Insecticide	toxic value (g/m ³)
DDT	5 - 10	Bassa (Baycarb)	17 - 30 - 44
Diazinon	12 - 18 - 32	Propoxur	18 - 30
Phoxim	7 - 12	Carbaryl	12 - 18
Chlorophoxim	12 - 20 - 32		

Example 11 Effectiveness against the termite species *Reticulitermes santonensis*

The toxicity against *Reticulitermes santonensis* of solutions containing the active compound I.3 in

chloroform having the concentrations mentioned in Example 10 was determined according to the detailed description of DIN EN 117 Edition 1981 which is concerned with the European standard method prescribed by the European Committee for standardization concerning wood preservatives, determination of the toxic value against *Reticulitermes santonesis*.

5 An outline of the method is as follows: (see DIN EN 117 for detail)

The same three wood-samples with impregnation treatment in vacuum as in Example 10 are provided.

They are exposed to 250 workers, 1 soldier and 1 nymph per batch for eight weeks, and afterword, the number of live/dead larvae is determined.

10 From this test, the toxic threshold value was between 0.135 g/m³ and 1.344 g/m³ of the active compound I.3.

The evaluation was made by the following standard:

*rating values:

0 = no attack

1 = attempted attack

15 2 = slight attack

3 = average attack

4 = strong attack

The results are shown in Table 5.

Table 5

Concentration of protect agent tested in % (m/m)	No. of wood sample	Quantity of solution absorbed per wood sample in g/m ³	Quantity of protective agent absorbed		Results of evaluation		
			per wood sample in g/m ³	average quantity absorbed in g/m ³	sur-viving workers %	Soldiers(S) or nymphs (N)	* rating
1.44x10 ⁻⁵ %	1	17.75	0.136	0.135	55	S/N	4
	2	17.47	0.134		51	S/N	4
	3	17.69	0.136		58	S/N	4
1.44x10 ⁻⁴ %	4	17.75	1.363	1.344	0	-	1
	5	17.39	1.336		0	-	1
	6	17.37	1.334		0	-	1
1.44x10 ⁻³ %	7	17.54	13.471	13.463	0	-	1
	8	17.56	13.486		0	-	1
	9	17.49	13.432		0	-	1
7.20x10 ⁻³ %	10	17.29	66.3936	68.211	0	-	0
	11	18.03	69.2352		0	-	0
	12	17.97	69.0048		0	-	0
1.44x10 ⁻² %	13	17.79	136.627	136.627	0	-	0
	14	17.72	136.090		0	-	0
	15	17.86	137.165		0	-	0
control samples diluent (chloroform)	16	17.72	0	0	50	-/N	4
	17	18.15	0		57	S/N	4
	18	17.77	0		48	S/N	4
control samples untreated	19	0	0	0	55	S/N	4
	20	0	0		62	S/N	4
	21	0	0		64	-/N	4

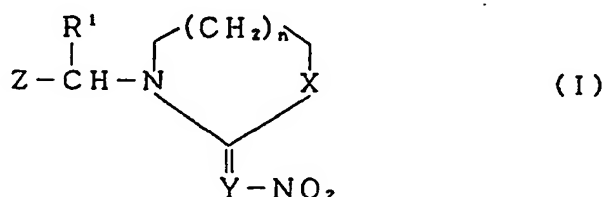
Comparative values of W. Metzner et al in "Holz als Roh- und Werkstoff," 35 (1977) 233-237, table 10 on page 236.

Table 6

Insecticide	toxic value g/m ³	Insecticide	toxic value g/m ³
DDT	> 1 500	Chlorophoxim	500
Dieldrin	50	Bassa	500
Lindan	75	Propoxur	140
Ethylparathion	200	Carbaryl	1 100
Phoxim	400		

Claims

1. Agents for preserving technical materials against insects, characterized in that they contain at least one compound of the formula (I)



wherein X is NH or S,

Y is CH or N

Z is 2-chloro-5-pyridyl or 2-chloro-5-thiazolyl,

R¹ is hydrogen or methyl, and

n is 0 or 1,

2. Agents according to claim 1,

wherein X is NH or S,

Y is CH or N,

Z is 2-chloro-5-pyridyl

R¹ is hydrogen, and

n is 0 or 1.

3. Agents according to claim 1, wherein the active compound is selected from the group consisting of

1-(6-chloro-3-pyridylmethyl)-2-nitromethyleneimidazolidine,

3-(6-chloro-3-pyridylmethyl)-2-nitromethylenethiazolidine,

1-(6-chloro-3-pyridylmethyl)-2-nitroiminoimidazolidine,

1-(6-chloro-3-pyridylmethyl)-2-nitromethylenetetrahydropyrimidine, and

3-(6-chloro-3-pyridylmethyl)-2-nitromethylenetetrahydro-2H-1,3-thiadine.

4. Agents according to claim 1, wherein technical materials are wood or composite wood-materials.

5. Agents according to claim 1, wherein insects are termites.

6. Process for preserving technical materials against insects, characterized in that the compounds of the formula (I) are allowed to act on said insects and/or their habitat.

7. Use of the compounds of the formula (I) for preserving technical materials against insects.

8. Process for the preparation of agents for preserving technical materials against insects, characterized in that the compounds of the formula (I) are mixed with extenders and/or surface active agents.

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9. Process for the preparation of agents for preserving technical materials against insects according to claim 8, characterized in that solvents and/or additional insecticides and/or fungicides are added.

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EUROPEAN SEARCH REPORT

Application Number

EP 92 10 6384

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 387 663 (BAYER) * Claims *	1-9	A 01 N 51/00 A 01 N 43/86
D,X	EP-A-0 163 855 (NIHON TOKUSHU NOYAKU SEIZO) * Pages 47-48; example 7; page 50; example 50; claims *	1-9	A 01 N 43/50 A 01 N 43/78 A 01 N 43/54 B 27 K 3/34
D,X	EP-A-0 192 060 (NIHON TOKUSHU NOYAKU SEIZO K.K.) * Page 111, lines 1-5; page 236; claim 4; examples 1,2; page 245; example 4 *	1-9	
X	EP-A-0 214 546 (NIHON TOKUSHU NOYAKU SEIZO) * Column 21, lines 45-51; claims *	1-9	
X	EP-A-0 256 407 (NIHON TOKUSHU NOYAKU) * Claims *	1-9	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			A 01 N B 27 K
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 15-07-1992	Examiner DALKAFOUKI A.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons * : member of the same patent family, corresponding document			